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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003901396 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION as filed on 25 March 2003.

WITNESS my hand this
Second day of April 2004

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Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s):

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

Invention Title:

"METHODS FOR BLEACHING OF CELLULOSIC MATERIALS"

The invention is described in the following statement:

A METHOD AND SOLUTION FOR BLEACHING CELLULOSIC MATERIALS

Technical Field

The present invention relates to a method and bleaching medium for bleaching cellulosic material. More particularly, the present invention relates to the use of an additive that improves the performance of non-chlorine bleaches, such as peroxide, oxygen and/or ozone.

Background of the Invention

Cellulosic materials such as cotton (in textile and other forms) and paper pulp are subjected to bleaching to increase whiteness.

Historically, chorine bleaching agents have been fairly widely used for this purpose, however these are now being phased out of use because of the adverse environmental impact of the release of organohalogens (AOX) during chlorine bleaching.

The alternative agents for use in bleaching cellulosic materials are peroxide (such as hydrogen peroxide), oxygen and ozone. Of these, peroxide is the most commonly used. Peroxide bleaching of cellulosic materials typically requires severe conditions including high temperatures, high alkali concentration, high chemical (bleaching agent) concentration and long exposure times. These operating conditions not only impose high energy costs, production costs and environmental damage, but they also lead to undesirable fibre and product performance.

There is currently an interest and demand for more effective non-chlorine based bleaching methods that are able to provide an adequate bleaching action under milder treatment conditions and thus minimise degradation of the desirable qualities of the cellulosic material.

To date, a number of methods have been proposed for achieving this. Generally these methods involve the use of a bleaching assistant, activator or agent to enhance the bleaching effect under milder treatment conditions. US patent nos. 4,392,979 and 5,034,096 describe methods for bleaching textiles and wood pulps using hydrogen peroxide assisted by cyanamide and derivatives thereof for improving the bleaching performance of hydrogen peroxide.

US patent nos. 6,248,209 and 6,342,124 describe methods of bleaching paper pulp using hydrogen peroxide or oxygen assisted by polyether compounds of a particular formula.

US patent no. 3,425,786 describes a method of bleaching textiles containing cotton using hydrogen peroxide assisted by N,N'-diacyl-methylene-diformamide.

US patent nos. 5,145,558 and 5,013,404 and European patent no. EP 0639666 describe methods of bleaching paper pulp using hydrogen peroxide assisted by quaternary ammonium compounds.

US patent no. H479 describes a method of bleaching paper pulp using hydrogen peroxide assisted by alkenylsuccinic anhydride.

US patent no. 5,912,404 describes a method of bleaching cotton and cotton blends using hydrogen peroxide assisted by potassium hydroxide.

In addition to the above examples, there is presently available a low temperature bleaching process for bleaching substrates containing cellulose using a hydrogen peroxide bleaching agent in combination with tetraacetylethylenediamine (TAED). TAED has poor water solubility which can prevent it from being used in some commercial applications.

All the above methods suffer from various drawbacks, one of them being that they are not sufficiently efficient and effective for industrial bleaching practice.

Numerous bleaching activators and peroxy acid bleaching precursors have also been developed to improve the stain removal capability of laundry detergents. The use of carboxylic acid ester peroxy acid precursors in laundry detergents has been described in Great Britain patent GB 836988, European patent EP0120591 and US patent no. 3,272,750. Other examples of peroxy acid precursors are quaternary ammonium compounds and cationic nitriles, both of which have been described in the context of laundry detergents in European patents EP0284292, EP0331229, EP0303520 and EP0458396. However, the peroxy acid bleaching precursors used in laundry detergents for improving stain removal are often not suitable for bleaching the full range of cellulosic materials such as paper pulps. Likewise, agents suitable for bleaching paper pulps are often not suitable for detergent use.

Accordingly, there is still a need for an alternative method and bleaching medium that is efficient and effective in industrial bleaching operations.

Summary of the Invention

According to the present invention there is provided a method of bleaching a cellulosic material comprising contacting the cellulosic material with a bleaching agent selected from peroxide, oxygen, ozone or a mixture thereof, in the presence of a guanidine-based additive.

Preferably the guanidine-based additive is in the form of a salt. The salts have very good water solubility which makes them particularly suitable for use in the present invention.

Although a large range of guanidine-based additives are effective, the preferred classes are the alkyl guanidines, acyl guanidines and the alkyl acyl guanidines. These guanidine-based additives perform especially well in enhancing the performance of peroxide,

oxygen and/or ozone bleaching agents in cellulose bleaching processes.

Aside from the guanidine-based additive, it has been found that a synergistic activation/acceleration effect can be achieved in the defined bleaching method when a peroxy acid precursor is used. The peroxy acid precursor is preferable one selected from O-acyl peroxy acid precursors, N-acyl peroxy acid precursors and cationic peroxy acid precursors including cationic nitriles. The present applicant has found that contacting the cellulosic material with the bleaching agent (preferably a peroxide), the guanidine-based additive and a peroxy acid precursor provides substantial enhancement in bleaching action with reduced chemical and energy consumption.

The present invention also provides a bleach activator composition for use in bleaching cellulosic material, the bleaching activator composition containing a guanidine-based additive and one or more components selected from the group consisting of stabilisers, buffers and surfactants.

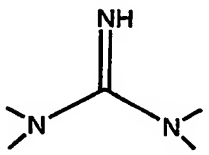
The bleach activator composition preferably also contains a peroxy acid precursor. This composition may be in the form of a solution, concentrate or solid. If in the form of a concentrate or solid, it can be diluted with water prior to use in the bleaching process.

The present invention also provides for the use of a guanidine-based compound as an additive in a bleaching process, or as a bleaching activator.

Detailed Description of the Invention

According to the method of the present invention, a guanidine-based compound is used as an additive in the bleaching process.

The term "guanidine-based additive" or "guanidine-based compound" is used in its broadest sense to refer to any compound containing the group:



It is noted that the amine nitrogen atoms illustrated may contain any substituent(as represented by the open-ended bonds), but the imine nitrogen atom is unsubstituted. The term encompasses guanidine ($NH_2C=NHNH_2$) itself, aromatic and aliphatic guanidines and derivatives thereof, as well as salts of the compounds containing the group illustrated above. The term also includes biguanide and derivatives thereof, which compounds also contain the group illustrated. However, where compounds containing a single guanidine unit only are intended, the term "monoguanidines" will be used to distinguish from the broader class of guanidines of which biguanide is a member.

Preferred guanidine-based additives are guanidine, alkyl-, alkenyl-, alkynyl- and aryl- guanidines and derivatives thereof, imino and acyl guanidines and derivatives thereof, and salts of the above.

Preferably the guanidine-based additive is in the form of a salt. Any organic or inorganic salt may be used, although for human health and safety reasons nitrate salts are not preferred. Examples of suitable salts are hydrochloride, sulphate, acetate and sulphonate.

A large number of guanidine-based compounds of a range of classes are commercially available. These include phenylguanidine / biguanide; halo-, alkyl- or alkoxyl- phenylguanidine/ biguanide; 1-benzylguanidine / biguanide; 1-benzoylguanidine and guanidine acetate.

Although a large range of guanidine-based additives are effective, the preferred classes are the alkyl guanidines, acyl guanidines and alkyl acyl guanidines.

These guanidine-based additives perform especially well in enhancing the performance of peroxide, oxygen and/or ozone bleaching agents.

By way of explanation, "alkyl guanidine" refers to a derivative of guanidine in which at least one amine hydrogen atom is replaced with an alkyl group. Unless otherwise indicated by the context, an alkyl guanidine, for example, can also be an acyl guanidine if another of the amine hydrogen atoms of guanidine is replaced with an acyl group. Such a compound may also be referred to as an alkyl acyl guanidine. It is also noted that the term "alkyl guanidine", for instance, encompasses dialkyl, trialkyl and tetraalkyl guanidine.

The term "alkyl" used either alone or in compound words such as "aralkyl" refers to straight chain, branched chain or cyclic hydrocarbon groups having from 1 to 10 carbon atoms, preferably 1 to 6 carbon atoms, more preferably 1 to 4 carbon atoms. Illustrative of such alkyl groups are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.

Preferably the alkyl group or groups are C1-C4 alkyl. More preferably, each alkyl group in the alkyl guanidines include 1 to 2 carbon atoms.

The term acyl guanidine is used to refer to guanidines containing at least one acyl group. Preferably the acyl group or groups attach directly to one or both of the two amine nitrogen atoms.

The term "acyl" denotes carbamoyl, aliphatic acyl group, acyl group containing an aromatic ring which is referred to as aromatic acyl or an acyl group containing a heterocyclic ring which is referred to as heterocyclic acyl having 1 to 20 carbon atoms, preferably 1 to 14 carbon atoms. Examples of acyl include carbamoyl; straight chain or branched alkanoyl, such as acetyl, propanoyl, butanoyl, 2-methylpropanoyl, octanoyl; alkoxycarbonyl, such as, ethoxycarbonyl,

cycloalkylcarbonyl, such as cyclohexylcarbonyl; alkylsulfonyl, such as methylsulfonyl; alkoxysulfonyl, methoxysulfonyl; aroyl, such as, benzoyl, toluoyl or naphthoyl; and aralkanoyl, such as phenylalkanoyl, for example, phenylacetyl.

More preferably each acyl group is benzoyl, acetyl or a derivative thereof.

Preferably the alkyl, acyl and alkyl acyl guanidines are monoguanidines.

The guanidine-based compounds may be unsubstituted or may be substituted by one or more substituents selected from alkyl, alkenyl, alkynyl, aryl, hydroxyl, alkoxyl, halo and amine. Where aryl groups are mentioned, the aryl group is preferably carbocyclic, such as phenyl, napthyl and so forth. The most preferred guanidine-based compounds contain no groups or substituents other than the alkyl and/or acyl groups.

Either one type or a mixture of guanidine-based additives can be used.

Any one or more of peroxide, oxygen and ozone can be used as the bleaching agent, however it is preferred for the bleaching agent to include peroxide. Hydrogen peroxide is the most commonly used peroxide. Others that containing a source of hydrogen peroxide, such as sodium peroxide, peroxy acids, sodium perborate and sodium percarbonate may also be used.

When oxygen is used as the bleaching agent, either oxygen gas, or oxygen-enriched air may be used, but oxygen gas is preferred.

It has been found that a synergistic activation/acceleration effect can be achieved in the defined bleaching method when a peroxy acid precursor is used. Peroxy acid precursors are reactive organic compounds that in alkaline solutions containing a source of hydrogen peroxide will generate the corresponding peroxyacid. The peroxy acid may be a peroxy carboxylic acid, a peroxy imidic acid, percarbonic acid, perboric

acid or similar. The conventional peroxy acid precursors contain an O-acyl or N-acyl group, such as N,N,N'N'-tetraacetylethylenediamine (TAED) and nonanoylbenzene sulphonate (NOBS). Other peroxy acid precursors are in the form of a cationic peroxyacid precursor (see for instance GB-A-1,382,594; US 4,751,015; EP-A-284,292 and EP-A-331,229), including cationic nitriles (see EP-A-303,520 and EP-A-458,396). The peroxy acid precursor is preferably one selected from O-acyl peroxy acid precursors, N-acyl peroxy acid precursors and cationic peroxy acid precursors including nitrile.

Any other additives known in the art can also be present during the bleaching process. Possible additives include stabilisers, surfactants, buffers and alkali sources. These are well known in the art of the invention. Other additives referred to in the description of the prior art set out above, including sulfonyl oximes, organophosphoric azide, sulfonylimidazole, cyanamide and disulfones may also be present. The additives used may have more than one function.

It is contemplated that the guanidine-based additive or combination of the guanidine-based additive with a peroxy acid precursor could be supplied in a pre-packaged form with other components. Such components may help to maintain the guanidine-based additive or the additive combination in a solution, mixture or suspension form, or in a state resistant chemical change. Examples of these additional components include surfactants, stabilisers and buffers.

The term "surfactant" refers to a chemical substance having detergency, foaming, wetting, emulsifying and/or dispersing properties. Surfactants are well known in the art of the invention.

The term "stabiliser" refers to an agent that controls the decomposition rate of the bleaching agent, and combines with metal impurities which may catalyse decomposition of peroxide and induce fiber damage.

Stabilisers are well known in the art of the invention. Examples of bleaching stabilisers are the inorganic stabilisers, such as sodium silicate and polyphosphates, and the organic stabilisers such as aminocarboxylates (diethylenetriaminepentaacetic acid), hydroxycarboxylates (glucoheptonic acid) and organophosphonates [ethylenediaminetetra(methylenephosphonic acid) and diethylenetriaminepenta(methylenephosphonic acid)]. The organic stabilisers are more preferable to use in the pre-packaged activator formulations. These are sometimes referred to as sequestering or chelating agents.

The term "buffer" refers to an agent that minimises the change in the pH of a solution when an acid or base is added to the solution. Examples of suitable buffers are sodium acetate/acetic acid, citric acid/sodium citrate, potassium hydrogen phthalate/HCl and citric acid/disodium hydrogen phosphate.

The invention can be implemented in most existing bleaching plants and processes that utilise hydrogen peroxide, oxygen or ozone with little or no alterations to the equipment of the plant. For instance, the present invention can be implemented with prior art methods known as "cold pad-batch", "pad-steam" and "exhaust" bleaching methods. These methods are particularly suited to bleach textiles and non-woven substrates containing cellulose.

The method of the present invention can be carried out over a broad range of operating conditions. The optimal operating conditions for the method will depend on, amongst other things, the precise nature of the substrate being bleached and the required properties of the final product.

Preferably, the guanidine-based additive is used in an amount of 0.1 - 5.0% by weight based on the amount of oven-dried pulp (in the case of bleaching cellulosic material in pulp form), or in the amount of 0.1 - 3.0 g/L of bleaching solution (in the case of bleaching cellulosic

material in textile form).

In the situation where the bleaching agent is peroxide, preferably the peroxide is used in an amount of 0.2 to 10.0% (more preferably 0.5-2.0%) by weight based on the amount of oven-dried pulp, in the case of bleaching cellulosic material in pulp form. In the case of bleaching cellulosic material in textile form, preferably the peroxide is used in the amount of 1.0-10.0 g/L (more preferably 2.0 - 6.0 g/L) of bleaching solution with the exhaust bleaching method, and 10.0-40.0 g/L (more preferably 15-25 g/L) with a cold pad-batch bleaching method.

In the situation where a peroxy acid precursor is also used, a preferred ratio of a peroxy acid precursor to the guanidine compound in the additive composition can range from 1:4 to 4:1. The ratio of 1:1 is most preferred.

The temperature at which the step of contacting the cellulosic material with the bleaching agent and guanidine-based additive is conducted may be from ambient to over 100°C. Preferably the temperature is between 40°C and 80°C.

The pH is preferably between pH 9.0 and 12.0 when bleaching with peroxide and oxygen.

Generally speaking, as the temperature of the bleaching method increases, the pH of the bleaching solution or medium agent can be reduced. For example, at a temperature increase from 60ºC to 80ºC, the pH can be reduced from 11.5 to 10.0.

The invention allows effective bleaching of substrates containing cellulose to be achieved using a bleaching agent containing hydrogen peroxide, oxygen or ozone over a broader range of pH and temperatures in comparison to the prior art methods. Importantly, the present invention allows bleaching of substrates containing cellulose to be carried out at relatively milder operating conditions which reduces energy and bleaching agent consumption and preserves desirable

qualities of the substrate being bleached.

The method can be conducted on the broad range of cellulosic materials in a range of forms, including textile, non-woven and pulp forms. The cellulosic materials/fibres may include cotton; regenerated cellulose fibres such as viscose, Tencel and cellulose acetate; bast fibres such as flax, hemp and jute; straw; wood fibres and paper pulps. Pulp can be derived from wood fibres, nonwood fibres (as mentioned above) and recycled fibres. The term "cellulosic material" encompasses mixtures and/or blends of these cellulosic fibres with other materials.

The term "bleaching medium" is used broadly to refer to a bleaching liquid, concentrate or solution. The bleaching medium of the present invention contains at least a bleaching agent selected from peroxide, oxygen, ozone or a mixture thereof, and a guanidine-based additive. These are described above in full with respect to the method of the invention.

Illustrative Examples

The present invention will now be described with reference to 7 non-limiting Examples.

Control solution

A control bleaching solution was prepared at room temperature and consisted of the following:

Silicate-free stabiliser	0.5-1.0 g/L
(Or Silicate stabiliser	2.0-3.0 g/L)
Surfactants	2.0 g/L
H_2O_2 (50%)	5.0 - 10.0 g/L
NaOH	1.0 - 2.0 g/L
Water	balance

(The units g/L represent grams of compound per litre of bleaching solution)

The silicate-free stabiliser used was a commercial product available from Böhme called Stabilisator 9188. The silicate stabiliser used was a commercial product named Stabicol BAC (Ciba). Leonil JDZ and/or Hostapur SAS 60 (Clariant) was used as the surfactant

Procedure

Each Example consisted of a set of trials that involved bleaching a cellulosic material with the control bleaching solution, and bleaching solutions of the present invention. The bleaching solutions of the present invention were made by adding a guanidine-based additive of the present invention to the control solution.

Examples of the guanidine-based additives of the present invention investigated included the following:

1,1-dimethylguanidine sulphate	(DMG)
N,N,N'N'-tetramethylguanidine sulphate	(TMG)
1-Methylguanidine hydrochloride	(MG)
1-Ethylguanidine sulphate	(EG)
1,1-diethylguanidine sulphate	(DEG)
1-benzoylguanidine hydrochloride	(BOG)
1-Acetylguanidine	(ATG)
1,1-dimethylbiguanide hydrochloride	(DMBG)
1-phenylbiguanide	(PBG)

In addition, in order to demonstrate the effectiveness of the present invention over the prior art bleaching solutions that include additives other than guanidine-based additives, the trials also included some samples where the substrate was bleached with the control solution containing the additives of the prior art. The prior art additives investigated in comparison to the additives of the present invention were N,N,N'N'-tetraacetylethylenediamine (TAED) and nonanoylbenzene sulphonate (NOBS).

The bleaching trials were conducted on a Mathis Labomat at a solution to substrate ratio of 20:1 (ie. 20 millilitres of solution per gram of substrate). The

solution and substrate were heated to a preselected temperature in the Mathis Labomat and held at that temperature for a period of 60 minutes. Upon completion of the 60 minutes, the substrate was rinsed with water, dried, and its brightness measured using a GretagMacbeth Color-Eye 7000A Spectrophotometer.

The trials were carried using 3 types of cellulosic substrates, namely an unscoured knitted cotton fabric, a woven fabric blend containing cotton and jute, and wood pulp.

EXAMPLE 1

Trial No.	Additive(g/L)		NaOH (g/L)	Final pH	CIE Whiteness
	DMG	TAED			
1	-	--	1.0	11.16	61.8
2	1.5	-	1.0	10.95	66.6
3	-	1.5	1.0	10.76	62.0
4	-	-	2.0	11.54	65.0
5	1.5	-	2.0	11.46	69.6
6	-	1.5	2.0	11.33	68.8

Trial nos. 1 and 4 were carried out using the control solution, i.e. no additive. Trials nos. 2 and 5 were carried out using a solution of the present invention containing DMG. Trials nos. 3 and 6 were carried out using the prior art solution containing TAED. Each of the trials occurred at 60°C on a cotton fabric substrate.

As can be seen, the whiteness of the substrate using the bleaching solution of the present invention was greater than the whiteness achieved using the control solution and prior art bleaching solution.

EXAMPLE 2

Trial No.	Reaction Temp	Activators Used	Final PH	CIE Whiteness
1	40°C	Control (no activator)	11.65	47.8
2		2 g/L DMG	11.64	53.6
3		1 g/L TAED+1g/L DMG	11.51	57.5
4	50°C	Control (No activator)	11.55	56.1
5		2 g/L DMG	11.49	62.5
6		2 g/L TAED	11.25	61.2
7		1 g/L DMG+1 g/L TAED	11.30	65.4
8	60°C	Control (no activator)	11.54	65.0
9		2.0 g/L DMG	11.40	70.6
10		2.0 g/L TAED	11.10	69.3
11		0.5 g/L TAED+0.5 g/L DMG	11.37	71.0
12		1.0 g/L TAED+1.0 g/L DMG	11.26	73.5

Trial nos. 1, 4 and 8 were carried out using the control bleaching solution. Trial nos. 6 and 10 were carried out using the prior art bleaching solution containing TAED additive. Trials nos. 2, 5 and 9 were carried out using bleaching solutions of the present invention. Trial nos. 3, 7, 11 and 12 were carried out using solutions of a preferred embodiment of the invention containing a guanidine-based additive and a peroxy acid precursor TAED. The trials were carried out at varying temperatures on a cotton substrate.

In addition to the superior bleaching performance achieved in trials 2, 5 and 9, the results of Example 2 show that the whiteness achieved using a bleaching solution containing mixtures of both DMG and TAED is greater than the whiteness achieved when only DMG or TAED

is added to the bleaching agent.

EXAMPLE 3

Trial No.	Activator	Final pH	CIE whiteness
1	Control (no activator)	10.69	61.9
2	2.0 g/L NOBS	10.52	67.7
3	2.0 g/L DMG	10.57	68.6
4	0.5 g/L NOBS + 0.5 g/L DMG	10.61	69.1
5	1.0 g/L NOBS + 1.0 g/L DMG	10.51	70.7

Trial nos. 1 and 2 were carried out using the control and prior art bleaching solutions, respectively. Trial no. 3 was carried out using a bleaching solution of the present invention. Trial nos. 4 and 5 were carried out using the preferred bleaching solution of the present invention containing mixtures of both DMG and the peroxyacid precursor NOBS. Each of the trials were conducted at 60ºC on a cotton substrate.

As can be seen, trials nos. 3 to 5 produced a whiter substrate.

EXAMPLE 4

Trial No.	Activator (1 g/L)	CIE Whiteness
1	Control (no activator)	61.6
2	TAED	63.2
3	MG	64.0
4	DMG	66.8
5	TMG	67.2
6	EG	63.5
7	DEG	63.5
8	DMBG	65.0
9	PBG	63.8

Trial nos. 1 and 2 were carried out using the control solution and the prior art solution containing TAED. Trial nos. 3 to 9 were carried out using a bleach solutions of the present invention containing various guanidine-based compounds. The trials were carried out at 60ºC on a cotton substrate.

As can be seen, the whiteness of the substrate achieved using the solution of the present invention is greater than the whiteness achieved by the control and prior art bleaching solutions.

EXAMPLE 5

Trial No.	Activator	CIE Whiteness
1	Control	61.1
2	0.2 g/L BOG	64.6
3	0.5 g/L BOG	65.9
4	0.5 g/L ATG	65.5

Trial nos. 1 was carried out using the control solution. Trial nos. 2 to 4 were carried out using bleach solutions of the present invention containing relatively low concentrations of BOG and ATG. The trials were carried out at 60ºC on a cotton substrate.

The trials demonstrate that these acylguanidines significantly enhances peroxide bleaching of cotton even at such low concentrations.

EXAMPLE 6

Trial No.	Activator (1 g/L)	CIE Whiteness	Berger 76 Whiteness	Brightness T452 (1987)
1	Control	4.3	15.9	55.9
2	DMG	9.4	19.4	57.8
3	TMG	10.1	20.2	57.8

Trial nos. 1 was carried out using control bleaching solution. Trial nos. 2 and 3 were carried out using bleach solutions of the present invention. The substrate used this Example was a cotton/jute blend and the trials were conducted at 60°C.

It is noted that the quality of the bleached substrate has been determined using three different scales and standards, namely the CIE, Berger and T452 scales.

EXAMPLE 7

Trial No.	Activator	Final pH	Brightness T452(1987)
1	Control	11.0	55.7
2	DMG(2g/L)	10.87	60.3

Trial nos. 1 and 2 were carried out on a paper pulp at 60°C. The trials demonstrate the bleaching solution of the present invention also provides superior bleaching of paper pulps.

The above Examples have been included in the specification for illustrative purposes only and are by no means to be taken as limiting the scope of the present invention.

Dated this 25th day of March 2003

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